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Acidification of Water by CO₂

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Abstract

In the 17th EIKE Conference (IKEK-17) Will Happer summarised a recently published paper *Acidification of Water by CO₂*, [1] by the four authors, which gives a quantitative discussion of why increasing concentrations of atmospheric CO₂ will not cause harmful acidification of natural waters on Earth and will likely benefit aquatic organisms. The reason is that alkalinity and dissolved CO₂ give high buffering capacity to most natural waters and minimize the change of pH from external influences.

Keywords: Ocean acidification; pH; alkalinity; buffering; carbonate chemistry.

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1. Introduction

Natural surface waters and rainwater contain dissolved CO₂, in equilibrium with atmospheric CO₂. As atmospheric CO₂ concentrations increase, the increase of the dissolved weak acid, CO₂, will lower the pH of the waters. Fig. 1, taken from reference [1], shows how the pH values of freshwater and seawater depend on the atmospheric partial pressure P of CO₂. The decrease of the pH of seawater from doubling the CO₂ partial pressure P at a temperature of $T = 25$ C would reduce the pH by $\Delta\text{pH} = -0.25$. The doubling would take more than a century at the current rates of CO₂ increase.

2. Sea Surface pH

Fig. 2, taken from the work of Hofmann *et al.* [2], shows the pH from doubling atmospheric CO₂ concentrations is comparable to, or smaller, than typical day-night fluctuations of pH in biologically active parts of the ocean, like coral reefs. Photosynthesis converts dissolved inorganic CO₂ into organic carbon in the tissues of living organisms. During the day, photosynthesis removes CO₂ faster than it can be replaced by eddy diffusion from the atmosphere above or from deeper water below. With less of the dissolved weak acid CO₂, less of the natural alkalinity of the seawater is cancelled and the pH can increase by several fractions of a pH unit, or more. During the night, aerobic respiration by living organisms converts organic compounds back to dissolved inorganic CO₂, and this approximately cancels the daytime pH increase.

Fig. 3, taken from work by Byrne *et al.* [3], shows the pH of the North Pacific Ocean, measured in the year 2006 along the longitude 152 ° W between Hawaii and Alaska.

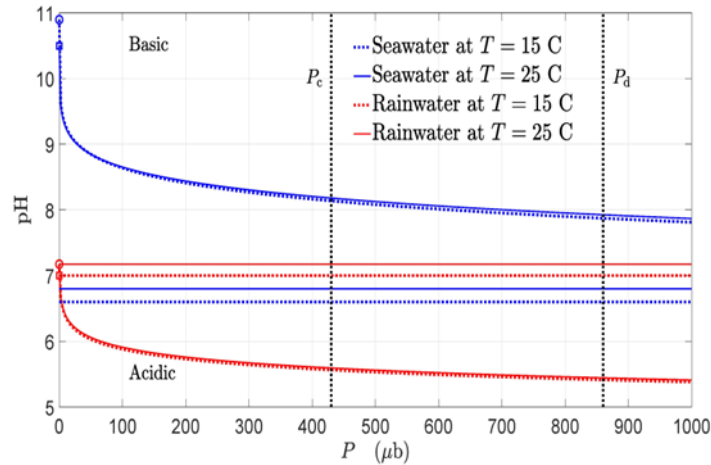


Figure 1: The curved lines are pH values of seawater (blue) and rainwater (red) in equilibrium with atmospheric partial pressure P of CO₂. In 2025, the pressure was $P_c = 430 \mu\text{b}$. The doubled value is $P_d = 860 \mu\text{b}$. Representative seawater has a salinity $S = 35 \text{ ‰}$, an alkalinity $[A] = 2.4 \text{ mM}$ and a boron molality $[B] = 0.43 \text{ mM}$. Rainwater contains only dissolved CO₂. The horizontal lines are neutral pH values, pH_n , when $[\text{H}^+] = [\text{OH}^-]$, for the four combinations of salinity and temperature. Only for freshwater at temperature $T = 25$ is neutral $\text{pH}_n = 7$.

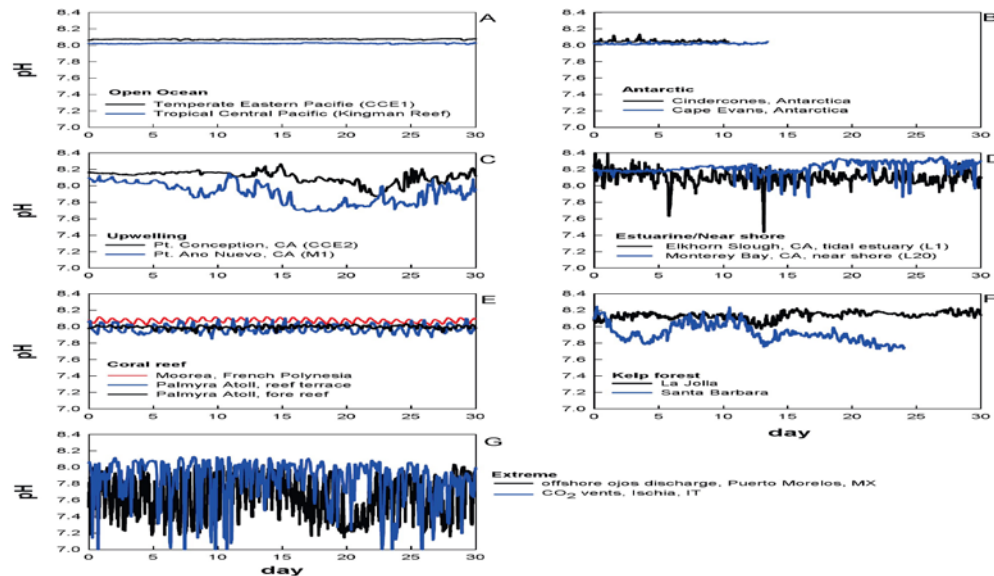


Figure 2: Time dependence of the pH of ocean surface waters from [2]. The very small pH decrease, 0.25 units from doubling atmospheric concentrations of CO₂, shown in Fig. 1, is smaller than the day-to-night fluctuations of pH in biologically active parts of the ocean.

The decrease of the pH with moderate depths below the surface is mostly due to the increase of dissolved inorganic carbon (DIC) as a result of the biological pump, the aerobic decomposition of sinking organic debris created by photosynthesis at the surface, and the dissolution of biomineralized parts at depths below the lysocline. The decrease of surface pH with increasingly

northerly latitudes is due to the decrease in alkalinity, [A], which is correlated with the decrease in surface salinity. Much of the very deep water of the North Pacific comes from cold, salty water that was formed off of Antarctica and other parts of the globe.

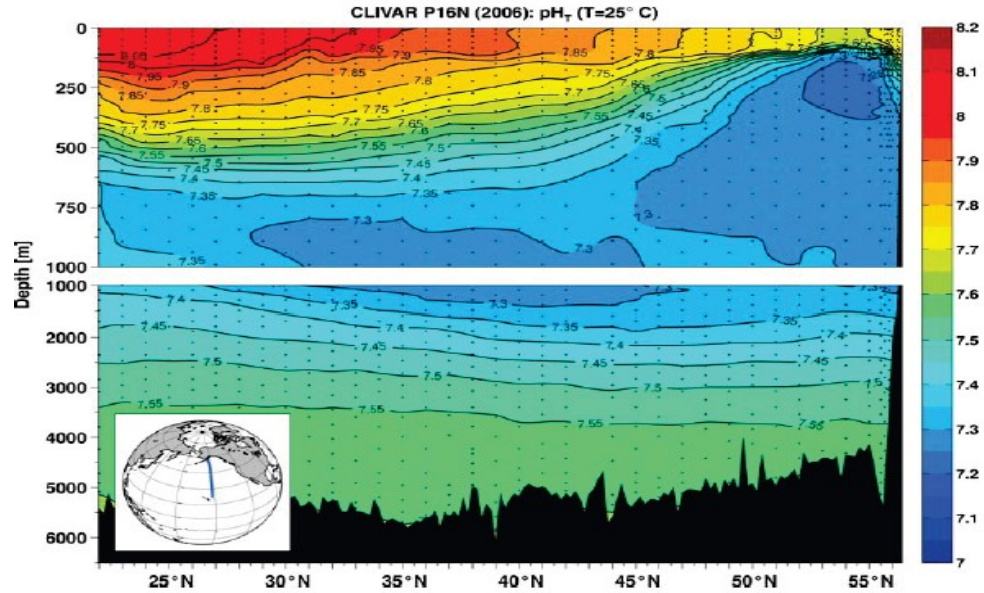


Figure 3: The pH of the North Pacific Ocean [3] along the longitude 152° W in 2006. The pH changes with latitude and depth are much larger than the pH change $\Delta pH = -0.25$ shown in Fig. 1 for doubling the atmospheric concentration of CO₂.

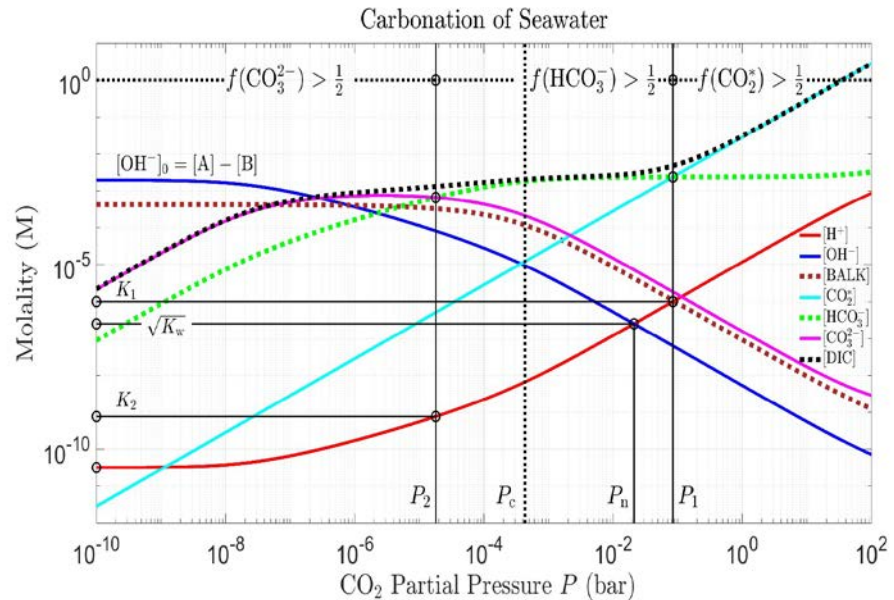


Figure 4: The molalities $[CO_2^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ of dissolved CO₂, and their sum [DIC] are plotted versus the partial pressure P of atmospheric CO₂ which is in equilibrium with seawater at a temperature $T = 25$ C. The contemporary partial pressure of CO₂ is $P_c = 430 \mu\text{bar}$.

Typical quantitative results of reference [1] are shown in Fig. 4. Shown, as a function of sea-level atmospheric partial pressure P of CO₂, are the molalities (moles per kilogram, M) of DIC,

including uncharged dissolved CO₂ molecules and sea-level undissociated carbonic acid H₂CO₃, denoted collectively as CO₂*, singly charged bicarbonate ions HCO₃⁻ and doubly charged carbonate ions CO₃²⁻. Also shown are the hydrogen-ion and hydroxyl-ion molalities, [H⁺] and [OH⁻], and the boron alkalinity [BALK]=[B(OH)₃+4] from boric acid, the second most abundant weak acid in seawater, after CO₂. At the contemporary partial pressure P_c of CO₂, large increases in P causes relatively small increases of [DIC].

3. Conclusion

We have in the referenced paper [1] reviewed the inorganic carbonate chemistry of natural waters, seawater, groundwater and rainwater, in equilibrium with the partial pressures P of CO₂ in the atmosphere. We have shown that even very large changes of P , like doubling from $P_c = 430 \mu\text{b}$ to $P_d = 860 \mu\text{b}$, change the pH of natural waters less than the day-to-night changes due photosynthesis of aquatic organisms, or due to local variations of seawater alkalinity. The pH changes are so small that any credible future increases of atmospheric CO₂ will cause no harm to aquatic life.

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